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Sorption of divalent heavy metal ions onto functionalized biogenic hydroxyapatite with caffeic acid and 3,4-dihydroxybenzoic acid

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Abstract

The sorption ability of biogenic hydroxyapatite (BHAP) towards heavy metal ions (Pb, Cu, Ni, Cd, and Zn) is compared with functionalized BHAP powders with caffeic acid (CA) and 3,4-dihydroxybenzoic acid (3,4-DHBA). The functionalization of the BHAP with either CA or 3,4-DHBA is indicated by the appearance of the colored powders due to the formation of the interfacial charge transfer (ICT) complexes. The detailed characterization of as-prepared and functionalized BHAP samples was performed using transmission electron microscopy, reflection spectroscopy, thermogravimetric analysis and determination of zeta potential. All three sorbents

clearly displayed preferential sorption of Pb ions when the total concentration of multi-component equimolar solutions of heavy metal ions is high. It should be emphasized that the sorption capacity of functionalized BHAP with either CA or 3,4-BHAP was found to be higher, up to 60%, compared to as-prepared BHAP without the decrease of selectivity towards Pb ions.

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Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) exhibits unique physicochemical properties thanks to which it has a wide range of applications in biomedicine, environmental remediation, materials science, catalysis, chromatography, *etc*. [1-4] The potential of calcium, phosphate and hydroxyl ions in the crystal lattice of HAP to be replaced with a variety of ions present in surrounding media gave a burst to investigations of the potential use of HAP as a sorbent in separation processes. [5,6] Although the ability to control the physicochemical properties of HAP by choosing synthetic routes and conditions is an advantage in specific fields of research and application, the amounts of material required for the practical utilization of HAP in pollution prevention, water treatment and soil remediation justify the use of naturally available HAP forms (geological, biogenic) over the synthetic ones.

Compared to geological deposits of phosphate rock, [7] animal bones have gained increased attention as a natural source of HAP due to more favorable properties, i.e., the trace-level concentrations of potentially toxic elements, the nano-size and large specific surface area of biogenic HAP (BHAP) crystals. [8] Besides, phosphate rock is on the European Commission List of critical raw materials, [9] while the biogenic waste is marked as the most important secondary source of phosphorous. [10] Therefore, the transformation of waste animal bones from growing meat industry into the sorbent material is highly encouraged.

In the course of BHAP preparation, organic phase can be removed from bone matrix by chemical treatments (nitric acid, sodium hydroxide, hexane, alcohol, hydrogen peroxide), [11-13] thermal treatments at different annealing temperatures and conditions, [12,14] as well as combining chemical and thermal treatments. [15,16] Isolated BHAP exhibited a larger specific surface area and the reactivity in comparison to the bone composite, which led to enhanced capacities of sorption. [11-15]

Further enhancement of the sorption capacity and/or selectivity can be achieved by proper functionalization of HAP with organic molecules, to provide novel surface centers of metal complexation. Although surface modification is widely investigated strategy in HAP biomedical applications (protein separation, drug delivery, cell scaffold, etc.), [17] such approach has rarely been used to modify the performance of HAP in metal separation processes. So far, encouraging results have been reported for amino-functionalized BHAP with salicylate-type of ligand (5-aminosalicylic acid) in the separation of Pb and Cu ions from contaminated water. [18] Hydroxyapatites with incorporated organic aspartate and glutamate anions have shown increased Pb sorption capacity in comparison to the untreated sample. [19] Furthermore, organo-apatites prepared by in situ incorporations of adipic acid, citric acid and

nitrilotris(methylene)triphosphonic acid, with organic content in the 2–8 wt.-% range, exhibit faster sorption rate and higher sorption capacity for Pb in acidic solutions compared to the pure apatite. [20] However, an attempt to improve sorption capacity and selectivity towards heavy metal ions of either synthetic or biogenic HAP by their functionalization with catecholate-type of ligands has never been made. A study of catechol adsorption on HAP was previously performed to evaluate how effective it may be in medical and dental adhesives. [21] It was shown that catechol, and molecules containing catechol groups, have higher rates and energies of adsorption to HAP than alcohols, amines, and carboxylic acids. Recently, the reactivity of HAP-based sorbents for the removal of catechol as a model organic pollutant from an aqueous solution was found promising, with the highest sorption capacity of 15 mg of C per gram of zinc-doped HAP sorbent. [22]

Functionalization of inorganic nanoparticles (mainly wide-band-gap oxides) with small organic molecules (catechol derivatives) so far has been used to prepare inorganic-organic-hybrids with improved optical properties due to the formation of the interfacial charge transfer (ICT) complexes. [23-30] This simple synthetic procedure is based on the condensation reaction between hydroxyl groups from the nanoparticles' surface and adjacent hydroxyl groups from ligand molecules and consequent formation of metal-oxygen-carbon-linkage. Therefore, it can be reasonably assumed that such a reaction will result in modified sorption characteristics of the material.

This study is the continuation of our efforts to improve the sorption ability of biogenic HAP towards heavy metal ions (Pb, Cu, Ni, Cd, and Zn) by proper functionalization. The advantage of the ICT complex formation, based on condensation reaction between surface hydroxyl groups from BHAP and adjacent hydroxyl groups from caffeic acid (CA) and 3,4-dihydroxybenzoic

acid (3,4-DHBA), was taken to prepare carboxy-functionalized sorbents with carboxylic groups separated at different distances from the surface of the inorganic support. The as-prepared BHAP, as well as functionalized BHAP with CA and 3,4-DHBA, were thoroughly characterized using microscopic and spectroscopic techniques. Effects of surface modification of BHAP on sorption capacity and selectivity were studied in a series of batch experiments using five-component heavy metal mixtures in a wide range of concentrations.

Materials and methods

Synthesis of BHAP and its functionalization with 3,4-DHBA and CA

The BHAP was prepared from bovine bones using hydrogen peroxide to remove organic phase, as described elsewhere. [12]

The functionalization of BHAP with CA and 3,4-DHBA was performed by dispersing 100 mg of BHAP in 30 mL of the water solution containing previously dissolved ligand (58.5 and 50 mg of CA and 3,4-DHBA, respectively). The molar concentration of ligands was identical and the ratio between the amount of BHAP and initial concentration of ligands provide the condition for full surface coverage of BHAP. The dispersion was stirred overnight, and, after that, the powder was separated by centrifugation, thoroughly washed four times with deionized water to remove excess ligand, and finally dried in the vacuum oven at 40 °C. The successful surface modification is indicated by coloration of the powder. For the sake of clarity, the functionalized BHAP with CA and 3,4-DHBA will be labeled further in the text as CA/BHAP and 3,4-DHBA/BHAP, respectively.

Characterization of pristine and functionalized BHAP with 3,4-DHBA and CA

Microstructural properties of pristine and functionalized BHAP were studied using transmission electron microscopy (TEM). A JEOL JEM-2100 LaB6 instrument operated at 200 kV was used for TEM imaging. TEM images were acquired with a GatanOrius CCD camera at 2× binning.

Specific surface area and the average pore radius of mesoporous BHAP, calculated from the nitrogen adsorption-desorption isotherms according to the BET method, were determined in our previous study [18] and found to be 75.1 m^2/g and 13.2 nm, respectively.

The content of the organic phase in CA/BHAP and 3,4-DHBA/BHAP samples was determined by thermogravimetric analysis (TGA) using a Setaram Setsys Evolution-1750 instrument. The measurements were performed in the temperature range 25–1000 °C at a heating rate of 10 °C/min, in the dynamic air atmosphere (flow rate 20 cm^3/min).

Optical characterization of as-prepared BHAP, as well as functionalized BHAP with CA and 3,4-DHBA, was performed using diffuse reflectance measurements (Shimadzu UV–VIS UV-2600 spectrophotometer equipped with an integrated sphere ISR-2600 Plus).

Electrokinetic properties of BHAP, CA/BHAP, and 3,4-DHBA/BHAP particles were compared using zeta potential analyzer Malvern Zetasizer NanoZS. The dispersion samples (0.100 g in 20.00 mL of 10^{-2} mol/L KNO_3) were equilibrated in PVC vials for 24 h at room temperature by shaking, and the zeta potential values were recorded at equilibrium pH.

Sorption experiments

Cation sorption capacity and selectivity of as-prepared BHAP powder were compared with surface-modified BHAP powders with CA and 3,4-DHBA in a series of equilibrium batch experiments at ambient temperature (21±2 ^{0}C) by varying the concentration of the equimolar mixture of Pb, Cu, Ni, Cd, and Zn ions. Five-component water solutions were prepared from nitrate salts of investigated cations to obtain the total concentrations in the range $10^{-3} - 10^{-1}$ mol/L. The initial pH values of obtained solutions were adjusted to 5.0±0.2 by adding minimum amounts of 10^{-2} mol/L solutions of either HNO_3 or NaOH. The sorbents and solutions were mixed in 50 mL centrifuge tubes at the constant solid-to-solution ratio (0.100 g in 20.00 mL) and shaken for 24 h on an overhead laboratory shaker at a speed of 10 rpm. Purified liquid phases were separated by centrifuging the suspensions at 9000 rpm for 7 minutes using Heraeus Megafuge 16. The equilibrium pH values were measured by WTW InoLab pH-meter, while the residual metal concentrations were determined using the Perkin Elmer 3100 Atomic Absorption Spectrophotometer (AAS). Sorbed amounts of each metal cation were calculated as the difference between its initial and final concentration.

Results and Discussion

Physicochemical properties of BHAP, CA/BHAP, and 3,4-DHBA/BHAP

The TEM data from as-prepared BHAP powders are presented in Figure 1. The TEM at low magnification (Fig. 1A) indicated the presence of agglomerated rod-like particles ((5–10)×(30–50) nm, diameter by length, respectively). The high-resolution TEM imaging revealed that the rod-like BHAP particles are crystalline (Fig. 2B) with resolved (211) lattice

fringes parallel to the rod axis. Analysis of the selected area electron diffraction (SAED) pattern (Fig. 1C) revealed the presence of the diffraction rings corresponding to (002), (211), (130), (222), (213), and (304) planes from the hexagonal phase of $Ca_5(PO_4)_3(OH)$ (Fig. 1D). Of course, functionalization of BHAP with either CA or 3,4-DHBA did not induce any morphological changes, and for the sake of clarity, those data are omitted.

The functionalization of BHAP with either CA or 3,4-DHBA is accompanied by the appearance of the pale-brown color of powders. The diffuse reflection spectra of unmodified BHAP, CA/BHAP, and 3,4-DHBA/BHAP powders in the wavelength range 300–1100 nm are shown in Figure 2 (curves a, b, and c, respectively). The as-prepared BHAP has absorption in the UV spectral region at energies higher than 3.35 eV. It is well-known that stoichiometric defect-free HAP is non-absorbing material in the visible as well as UV spectral region. [2] However, quantum chemical calculations based on density functional theory by Bystrov et al. [31] indicated that the presence of oxygen vacancy in the phosphate groups would lead to the energy band gap of about 3.45 eV. On the other hand, the CA/BHAP and 3,4-DHBA/BHAP samples are visible-light-responsive (see Fig. 2) with similar absorption properties (absorption onset at ~900 nm, i.e., ~1.4 eV). The absorption red-shift induced by functionalization of BHAP with CA and 3,4-DHBA is a consequence of the ICT complex formation. The similar effect was observed upon surface-modification of BHAP with salicylate-type of ligand (5-aminosalicylic acid). [18,32] Although the optical properties of surface-modified BHAP with CA and 3,4-DHBA is worthy of further investigation, it is not the main focus of this study.

It should be emphasized, based on the TGA results that the content of organic phases in both inorganic-organic hybrids is very small. The TGA curves of pristine and surface-modified BHAP are almost the same indicating that observed optical effects are induced by less than 3 wt.-% of

the organic phase (see Supporting Information, Fig. S1). Small changes of the zeta potential upon surface modification of BHAP with either CA or 3,4-DHBA/BHAP (see Supporting Information, Table S1) are in accordance with the low content of organic phase determined by TGA measurements. It is worth noting that in the inert electrolyte at equilibrium pH value all samples have negative surface charge (-10.3, -10.5, and -12.3 meV for BHAP, CA/BHAP, and 3,4-DHBA/BHAP, respectively) favorable for sorption of cationic species.

Due to the low concentration of organic components in CA/BHAP and 3,4-DHBA/BHAP samples, our attempt to confirm the mode of coordination between ligand molecules and BHAP using FTIR spectroscopy failed. Simply, complete disappearance of all vibration bands that belong to CA and 3,4-DHBA was observed upon their chemisorption onto BHAP powder. However, extensive literature data concerning the ICT complexes between various wide-band-gap oxides such as TiO_2 [23-27] and Al_2O_3 [29,30] and variety of catecholate-type of ligands strongly suggest that the ICT complex between BHAP and CA as well as BHAP and 3,4-DHBA is facilitated by the condensation reaction between surface hydroxyl groups from BHAP and adjacent hydroxyl groups from ligand molecules. To conclude, functionalization of BHAP with CA and 3,4-DHBA provide two sorbents with the same free functional group − carboxylic − placed at the different distances from the surface of the inorganic support.

Sorption properties of BHAP, CA/BHAP, and 3,4-DHBA/BHAP

The total sorption capacities of as-prepared and functionalized BHAP (CA/BHAP and 3,4-DHBA/BHAP) powders exposed to equimolar Pb, Cu, Ni, Cd, and Zn solutions, as well as corresponding equilibrium pH values are shown in Figure 3. Based on the sorption data, some

general features can be readily recognized. First, the total molar amounts of cations sorbed by BHAP, CA/BHAP, and 3,4-DHBA/BHAP from equimolar five-component solutions increases with the increase of the initial concentration of heavy metal ions, and the saturation is reached at high metal loadings. Second, the sorption capacities of as-prepared and functionalized BHAP powders towards heavy metal ions are similar at the low concentration end. However, when the concentration of heavy metal ions is sufficiently high, the enhanced sorption by CA/BHAP and 3,4-DHBA/BHAP can be noticed compared to as-prepared BHAP powder. For example, the total sorption capacity of 3,4-DHBA/BHAP is 60% higher compared to as-prepared BHAP for the highest initial concentration of heavy metal ions (10^{-1} mol/L). Third, the increase in metal sorption is accompanied by the decrease in equilibrium pH, and the enhancement of the sorption capacity of functionalized BHAP coincides with the low equilibrium pH values of multi-component solutions (pH $\leq$ 3.5). The lowering of pH is a consequence of cation sorption *via* complexation with protonated surface groups of both inorganic and organic components of the hybrid sorbents. [18,33]

In multi-component systems, sorption is influenced by the competition of the metal ions for the active surface sites. To evaluate the selectivity of as-prepared BHAP and functionalized BHAP with CA and 3,4-DHBA, the percentage of sorbed ions (Pb, Cu, Ni, Cd, and Zn) for the lowest and the highest total concentration of equimolar multi-component mixtures (10^{-3} and 10^{-1} mol/L, respectively) is presented in Figure 4. As expected, all three sorbents do not display selectivity when the total concentration of ions is low (10^{-3} mol/L) due to the presence of the excess of available surface sites. However, when the total concentration of divalent metal ions is high (10^{-1} mol/L) – higher than the number of available surface sites – all three sorbents display the selective sorption of Pb ions. The selective sorption of Pb ions by BHAP is in agreement with

literature data indicating that among divalent metal ions sorption of Pb is the most efficient due to its preferential removal by dissolution of HAP phase and precipitation of less soluble hydroxypyromorphite. [5,6] Quite the opposite, the maximum sorption capacity for Pb was the lowest with respect to Zn, Cu, Cd, Ni, and Co when non-apatite phosphate sorbent was used. [34] It should be emphasized that the higher sorption capacity of functionalized BHAP samples did not diminish their selectivity towards the Pb ions (Fig. 4B). In fact, stability constants measured for the formation of 1:1 complexes between divalent metal ions and different carboxylate anions, including benzoic acid, follow the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$, [35] which coincides with the selectivity of modified BHAP samples. The similar preference of Pb sorption was observed for amino-functionalized BHAP in equilibrium experiments with bi-component solutions of Pb and Cu ions. [18]

The isotherms of sorption of each component from equimolar five-component solutions (Pb, Cu, Ni, Cd, and Zn ions) by BHAP, CA/BHAP, and 3,4-DHBA/BHAP are shown in Figure 5 (A, B, and C, respectively). It is clear that sorption of Pb ions by as-prepared BHAP, as well as functionalized BHAP with either CA or 3,4-DHBA, is significantly more pronounced compared to all other investigated ions. Except for Pb, the sorption patterns of studied ions by all three sorbents exhibit a maximum followed by declining or irregular shape of isotherms with the increase of C_e. Such forms of isotherms are generally associated with sorption of less competitive species from the mixture. [18,36] Namely, as long as the active surface sights are not completely saturated, sorption of Cu, Ni, Cd, and Zn ions is not suppressed by the sorption of Pb ions, but, at high initial concentrations of the mixture, a residual amount of Pb ions in solution inhibits their further sorption. There is also a competition between the other cations so that Cu

and Cd sorption is still measurable while Ni and Zn removal is negligible at higher concentrations of the mixture.

Obviously, the obtained data for sorption of Cu, Ni, Cd, and Zn ions, due to irregular Q_e *versus* C_e dependence, could not be fitted to any isotherm with acceptable correlation coefficients. The sorption patterns of Pb ions were fitted by Langmuir [37] and Freundlich [38] isotherm models (Equations 1 and 2):

$$C_e/Q_e = 1/(Q_{max}K_L) + C_e/Q_{max} \qquad (1)$$

$$log\ Q_e = log\ K + 1/n\ log\ C_e \qquad (2)$$

where Q_e (mmol/g) and C_e (mmol/L) represent the equilibrium concentration of Pb ions in the solid and in the liquid phase, respectively, Q_{max} (mmol/g) is the maximum sorption capacity, K_L (L/mmol) represents the Langmuir sorption constant, whereas K ($mmol^{1-1/n}\ L^{1/n}g^{-1}$) and $1/n$ are the Freundlich model parameters related to the sorption capacity and affinity. From the linear fits (see Supporting Information, Fig. S3), sorption parameters are calculated and summarized in Table 1.

Based on the obtained correlation coefficients, the isotherms of competitive Pb sorption generally fit better to the Langmuir than to the Freundlich model. The best correspondence to the Langmuir model has the sorption pattern of Pb ions by BHAP with a distinct plateau for high C_e values. Since Langmuir equation is based on the assumptions that sorption takes place on a homogeneous surface with formation of a monolayer, poorer correlation, obtained for the inorganic-organic hybrid samples may be an indication of Pb co-sorption by BHAP itself and the organic phase. At the same time, compared to BHAP, surface modified samples exhibit better correlation with Freundlich isotherm typical for sorbents having different active surface sites. Langmuir constant K_L decreases in the sequence: BHAP, CA/BHAP, 3,4-DHBA/BHAP,

indicating that modified samples have a higher capacity but lower affinity for Pb than the pure BHAP. The shape of cation sorption isotherms on various apatite-based composites was found to be complex, demonstrating that there are different functional groups on the surface which can take action as sorption sites. [39,40]

It is well-known that HAP samples of different origin or heaving different treatment history exhibit different selectivity. For example, similar to the results presented in this study, the preferential sorption of Pb ions has been reported by functionalized BHAP, [18] as well as multi-walled carbon nanotubes, [41] with 5-aminosalicylic acid. On the other hand, higher sorption capacities were reported for Cu with respect to Pb ions using sorbents produced by pyrolysis of cow bones. [42] Also, the strong inhibitory effect of Cu ions on Pb sorption by HAP was reported by Ma *et al.* [43] To briefly conclude, preferential sorption of Pb ions from the multi-component solutions indicates that BHAP might have potential use as a sorbent for selective removal of Pb ions from multi-component heavy-metal ions solutions. In addition, functionalization of BHAP with a small amount of adequately chosen ligands (CA and 3,4-DHBA) lead to significant increase of its sorption capacity (up to 60%), but, does not influence on its selectivity towards Pb ions.

Conclusion

The functionalization of BHAP with catecholate-type of ligands (CA and 3,4-DHBA) lead to the formation of inorganic-organic hybrid materials with potential diverse applications including sorption, drug delivery, photo-driven catalytic reactions, *etc*. The main advantages of the proposed functionalization approach are simplicity and the formation of strong covalent bonds

between inorganic and organic part of hybrids. The sorption data indicate selective removal of Pb ions from five-component equimolar solutions of heavy metal ions (Pb, Cu, Ni, Cd, and Zn ions) by all three sorbents (BHAP, CA/BHAP, and 3,4-DHBA/BHAP). However, the sorption capacities of functionalized BHAP are higher compared to the unmodified one. It should be noted that the better sorption capacity was found for a hybrid sample where the free carboxylic group is closer to the surface of BHAP (3,4-DHBA/BHAP). Simply speaking, functionalization of BHAP with CA and 3,4-DHBA transformed the waste material into sorbent with improved capability for selective removal of heavy metal ions. The increase of the maximum sorption capacity up to 60%, observed for 3,4-DHBA/BHAP compared to unmodified BHAP, cannot be explained from the mechanistic point of view by the presence of organic phase solely. The content of the organic phase is too small. We can only assume that when the concentration of cations is higher than the number of available BHAP surface sites, there is a switch in the sorption mechanism in functionalized BHAP samples. Based on these preliminary results, it seems that systematic investigation of sorption ability of functionalized hydroxyapatite with a variety of multifunctional ligands is worthy of further study.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. TEM data from BHAP: (A) TEM image at low magnification, (B) high-resolution lattice image, (C) the SAED pattern (D) with corresponding planes from the hexagonal phase of $Ca_5(PO_4)_3(OH)$

Figure 2. Reflection spectra of BHAP (a), CA/BHAP (b), and 3,4-DHBA/BHAP (c) in UV–Vis–NIR spectral range

Figure 3. The total sorption capacities of BHAP, CA/BHAP and 3,4-DHBA/BHAP powders exposed to equimolar Cu, Pb, Ni, Cd, and Zn solutions and the corresponding equilibrium pH values, in relation to the total initial concentrations

Figure 4. The percentage of sorbed Cu, Pb, Ni, Cd and Zn ions from equimolar ion mixtures of total concentration (A) 10^{-3} mol/L and (B) 10^{-1} mol/L, at equilibrium with either BHAP or CA/BHAP or 3,4-DHBA/BHAP powders

Figure 5. The isotherms of sorption of each component from equimolar five-component solutions (Cu, Pb, Ni, Cd, and Zn ions) in various systems: (A) BHAP, (B) CA/BHAP, and (C) 3,4-DHBA/BHAP

Table 1. The parameters of Pb^{2+} equilibrium sorption from five-component equimolar mixtures calculated by Langmuir and Freundlich isotherm models
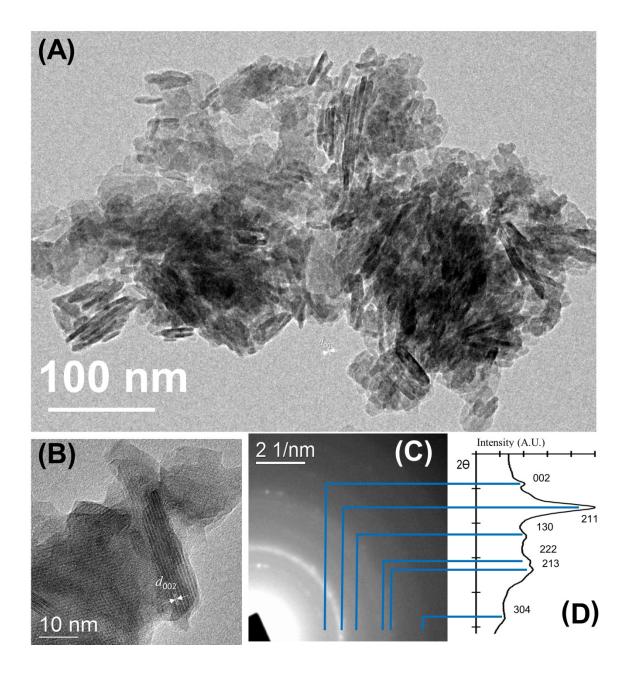
Sample	$Q_{max,exp}$ (mmol/g)	Langmuir model			Freundlich model		
		Q_{max} (mmol/g)	K_L (L/mmol)	R^2	K (mmol$^{1-1/n}$ L$^{1/n}$g^{-1})	$1/n$	R^2
BHAP	1.45	1.48	1.81	0.992	0.785	0.429	0.878
CA/BHAP	1.97	2.10	0.84	0.991	0.795	0.596	0.936
3,4-DHBA/BHAP	2.36	2.70	0.50	0.972	0.979	0.680	0.930

Figure 1. TEM data from BHAP: (A) TEM image at low magnification, (B) high-resolution lattice image, (C) the SAED pattern (D) with corresponding planes from the hexagonal phase of $Ca_5(PO_4)_3(OH)$
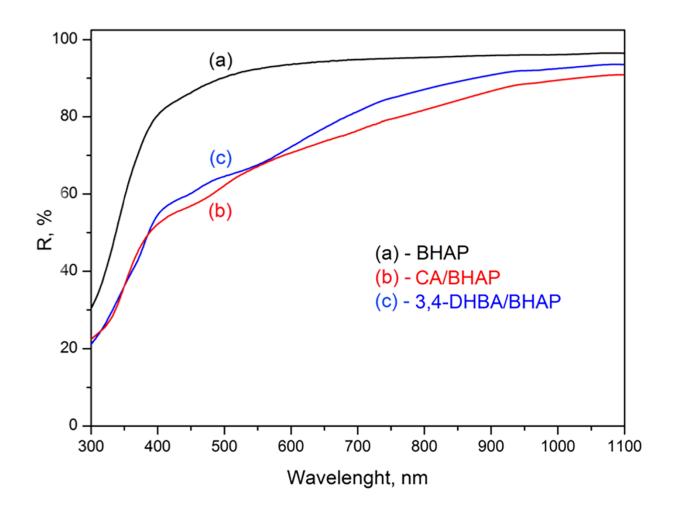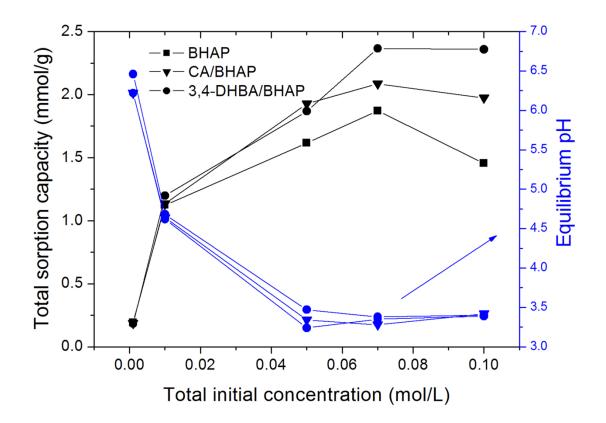
Figure 2. Reflection spectra of BHAP (a), CA/BHAP (b), and 3,4-DHBA/BHAP (c) in UV–Vis–NIR spectral range

Figure 3. The total sorption capacities of BHAP, CA/BHAP and 3,4-DHBA/BHAP powders exposed to equimolar Cu, Pb, Ni, Cd, and Zn solutions and the corresponding equilibrium pH values, in relation to the total initial concentrations
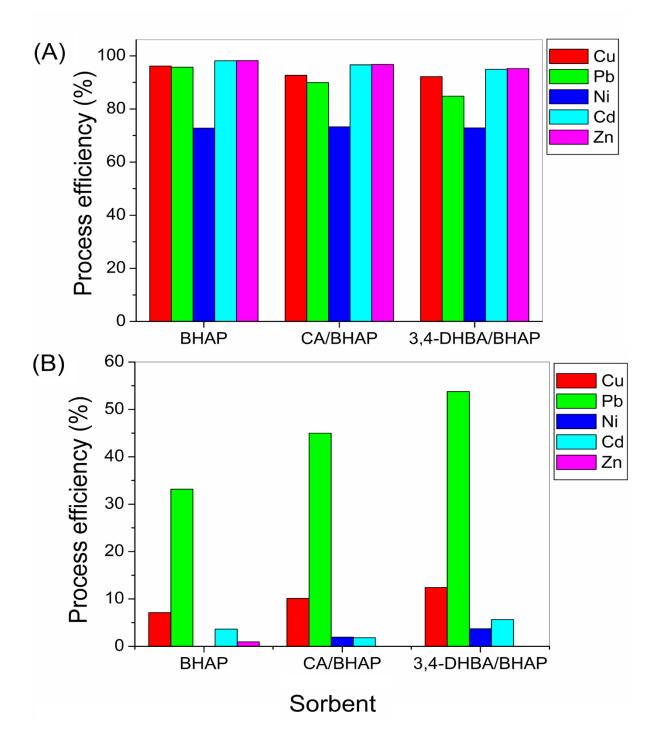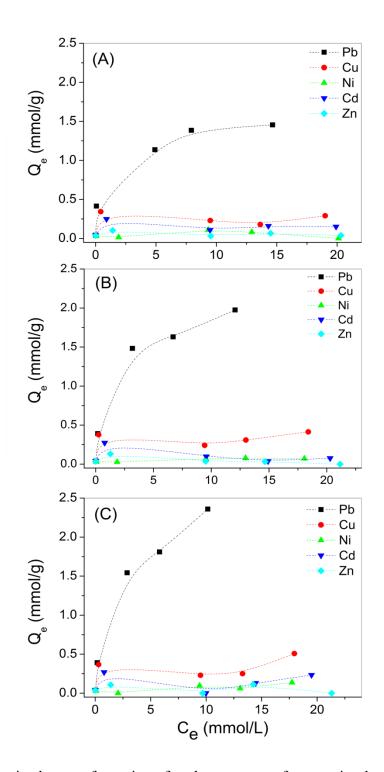
Figure 4. The percentage of sorbed Cu, Pb, Ni, Cd and Zn ions from equimolar ion mixtures of

total concentration (A) 10^{-3} mol/L and (B) 10^{-1} mol/L, at equilibrium with either BHAP or

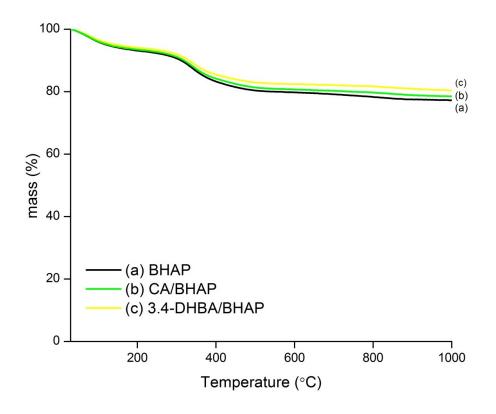CA/BHAP or 3,4-DHBA/BHAP powders

Figure 5. The isotherms of sorption of each component from equimolar five-component solutions (Cu, Pb, Ni, Cd, and Zn ions) in various systems: (A) BHAP, (B) CA/BHAP, and (C) 3,4-DHBA/BHAP

Figure 1S. The TGA data from as-prepared BHAP (a), CA/BHAP (b), and 3,4-DHBA/BHAP (c) powders obtained in the temperature range 25–1000 °C at a heating rate of 10 °C/ min, in the dynamic air atmosphere (flow rate 20 cm^3/min)

Table S1. Zeta potential of as-prepared BHAP, CA/BHAP, and 3,4-DHBA/BHAP powders

dispersed in the inert electrolyte (10^{-2} mol/L KNO_3, solid-to-solution ratio 1/200).

Sample	Equilibrium pH	Zeta potential (meV)
BHAP	7.5±0.1	-10.3 ± 0.6
CA/BHAP	7.2±0.1	-10.5 ± 1.4
3,4-DHBA/BHAP	7.3±0.1	-12.3 ± 1.0

Figure S2. Linear fits of Pb equilibrium sorption from five-component equimolar mixtures by BHAP, CA/BHAP, and 3,4-DHBA/BHAP using Langmuir (A) and Freundlich (B) isotherm models